Processing of leather waste: pilot scale studies on chrome shavings. Isolation of potentially valuable protein products and chromium

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Abstract

Hides come to the tanner as a by-product of the meat industry. The tanning process, in turn, generates much greater quantities of by-products and wastes than leather. One ton of wet salted hides yields only 200 kg of leather but over 600 kg of solid waste, or by-product if a market can be found. In the United States, nearly 60,000 metric tons of chromium-containing solid waste, i.e. chrome shavings, are generated by the leather industry each year, and approximately ten times this amount is generated worldwide. Land application for the disposal of chromium-containing tannery and other leather wastes has been widely practiced during most of the twentieth century, but fewer landfill sites can be found every day and the cost of transportation and disposal increases. Historically, these materials were used in the production of fertilizer or composite boards, but while once the company producing and marketing fertilizer or boards would pay for the waste and its transportation, nowadays, the tanner has to pay for such things. Over several years, we have demonstrated that it is possible to isolate protein products (gelatin and collagen hydrolysate) from chrome shavings by using an alkaline protease under mild conditions. The objective of the present work was to perform pilot plant trials to isolate protein products from chrome shavings, treat and purify the remaining chrome cake and tan hides with the recovered chromium. Because of the high nitrogen content, the isolated collagen hydrolysate has potential use as a fertilizer and in animal feed additives. The gelatin has potential use in cosmetics, adhesives, printing, photography, microencapsulation, films or even as an additive in finishing products for the leather industry. Published by Elsevier Science Ltd

1. Introduction

We know that "pollutants" are generated by all human activities, starting with the process of life itself. Primary, secondary and tertiary economic activities produce residues, which must be managed and treated adequately [1]. The environmental impact of leather manufacture is not the only one that is being legislatively restrained.

Hides come to the tanner as a by-product of the meat industry. The tanning process, in turn, generates even greater quantities of by-products and wastes than of finished leather [2]. An outline of the primary steps of the chrome tanning, the process by which hides or skins are converted into crust leather (tanned with chromium III) is presented in Fig. 1. The wastes generated during this process are highlighted in the step where they are produced. One metric ton of wet salted hides yields 200 kg of leather, along with about 250 kg of tanned solid waste and about 350 kg of non-tanned waste; 100 kg is lost in wastewater [3]. Thus, there are two dimensions to the waste/by-products problem that confront tanners: minimizing the quantity of waste generated and maximizing the return on by-products.

In the United States, almost 60,000 metric tons of chromium-containing solid waste are generated by the leather industry each year, and approximately 10 times this amount is generated worldwide. Land application

and disposal of solid, chromium-containing tannery wastes has been widely practiced during most of the twentieth century. This is a rather expensive and environmentally inappropriate way of handling a waste material that has the potential for reutilization. In addition, the costs of disposal will continue to increase as fewer landfill sites can be found and the cost of transportation increases. About 75% of the chromium-containing solid waste is produced when the tanned hide is shaved to a uniform thickness. These chrome shavings are small particles, in a variety of shapes, mainly consisting of collagen cross-linked with Cr(III) complexes. Historically, chrome shavings were used as fertilizers, but while once the fertilizer producer would pay for the waste and its transportation, nowadays, the cost of transport and disposal often is borne by the tanner.

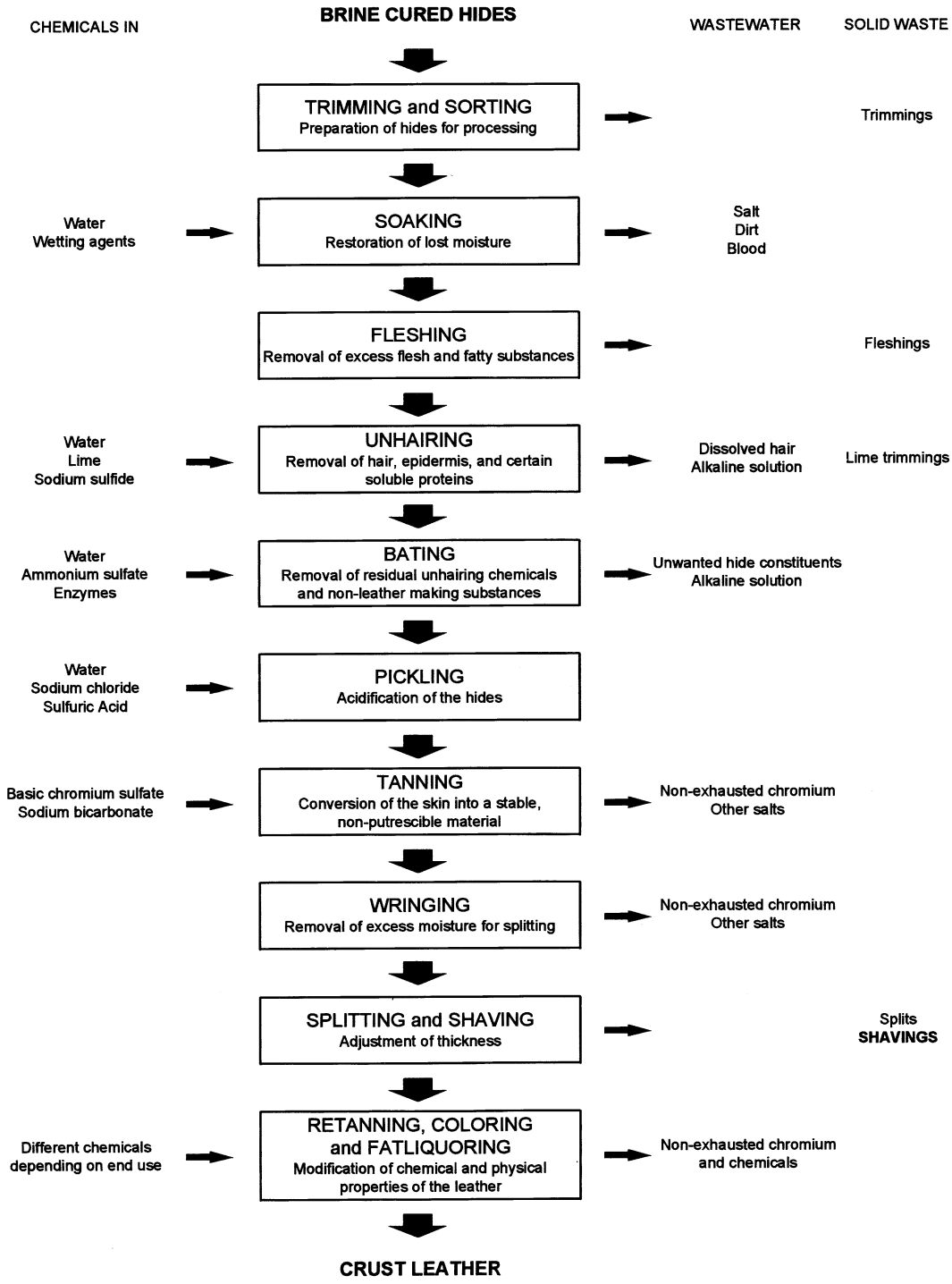


Fig. 1. Earlier steps of leather chrome tanning process. Further steps (drying, buffing, finishing and measuring) would be necessary to produce commercial leather.

Therefore, it is interesting to note the potential for profit from these solid chromium-containing tannery wastes. An earlier publication [4] from this laboratory includes a review of research into the processing and utilization of these wastes. Between 1969 and 1988, researchers around the world published and patented methods for hydrolyzing leather waste to recover amino acids and peptides for use in feeds and fertilizers. This time period also saw the development of methods for the recovery of chromium by wet air oxidation, peroxide treatments and incineration. Uses not requiring extensive pretreatment of solid leather waste, include the manufacture of insulators and building materials, composites for footwear or leather and paper substitutes.

Over several years, we have demonstrated the feasibility of isolating protein products from chrome shavings with the use of an alkaline protease under mild conditions. This process has been patented, broadly described, [4–6], and used worldwide with some modifications [7–10]. Most of the experiments reported were performed on a laboratory scale, where reproducibility was demonstrated [4]. The process has recently been scaled up for pilot plant and industrial trials [11–13]. The economics of the process have been demonstrated through the use of a computer-assisted process simulation and cost estimation [14]. The quality of the protein products isolated, that is, gelatin and collagen hydrolysate, has been studied and functional properties have been described [15–17] The objectives of recent pilot plant trials [12,13] were to determine the effects of scale on protein products isolated from chrome shavings, to treat and purify the remaining chrome cake, and to demonstrate the usefulness of recovered chromium.

2. Experimental

In our experience, analysis of chrome shavings from several commercial sources yielded the following relatively narrow ranges of values for: pH (3 to 4); moisture (50 to 54%); ash (8 to 14%); total Kjeldahl nitrogen, TKN, (14 to 16%); fat (0.1 to 1.8%) and chromium (3 to 4% as chromic oxide). If the pH of the shavings was outside of this range, it was adjusted to assure the success of the process; other values used to characterize the shavings are not critical.

2.1. Isolation of gelatin

Chrome shavings obtained from a commercial tannery were digested using our previously reported two-step process [4], outlined in Fig. 2. In the first step, the shavings were suspended in water such that 5 kg water was added for each kg of shavings, 0.1% non-ionic surfactant (Pluronic 25R2 from BASF, Parsippany, NJ) was added to prevent foaming. MgO, to a concentration of 6%, was added to increase the alkalinity to pH 8–9. Shavings, water, surfactant and MgO were tumbled at 16 rpm for 6 h in a Dosemat tanning drum (Dose Maschinenbau GmbH, Lichtenau, Germany) with the temperature controlled at 72°C. The reaction mixture was then filtered warm through a conventional filter press (Model AA Manual Filter Press, Serfilco, LTD., Glenview, IL) to separate the gelatin (filtrate) from the chrome sludge. The gelatin slurry—typically approximately 3 kg was obtained from the 6 kg starting mixture—was deionized batchwise using Ag® 501-X8 (D) mixed bed resin (Bio-Rad Laboratories, Hercules, CA) (5 g/100 ml of protein solution). The solution was stirred and additional resin was added until there was no further change in color of the resin. After treatment, the solutions were filtered through sintered glass funnels and lyophilized in preparation for chemical and physical analyses.

2.2. Isolation of collagen hydrolysate

In the second step, additional water (200%), surfactant (0.1%), MgO (2%) and alkaline protease (0.0125%, Liquid Alcalase^{R}, Novo Nordisk, Inc., Franklinton, NC) were added to the chrome sludge at 72°C, and this mixture was tumbled at 16 rpm for 1.5 h. The reaction mixture was then filtered warm through the filter press to separate collagen hydrolysate from the chrome cake. pH was monitored during the entire process, and adjusted to 9.0 as needed to maintain optimum alkalinity for avoiding chrome dissolution and promoting enzyme activity. These processes differed slightly from the lab scale process [4]. For example, at the pilot scale the process was run in a Dosemat drum where between 30 min and 1 h were required to heat a mixture to 72°C. The real time for each step in the pilot process thus was longer than at the laboratory scale.

2.3. Isolation of chromic oxide

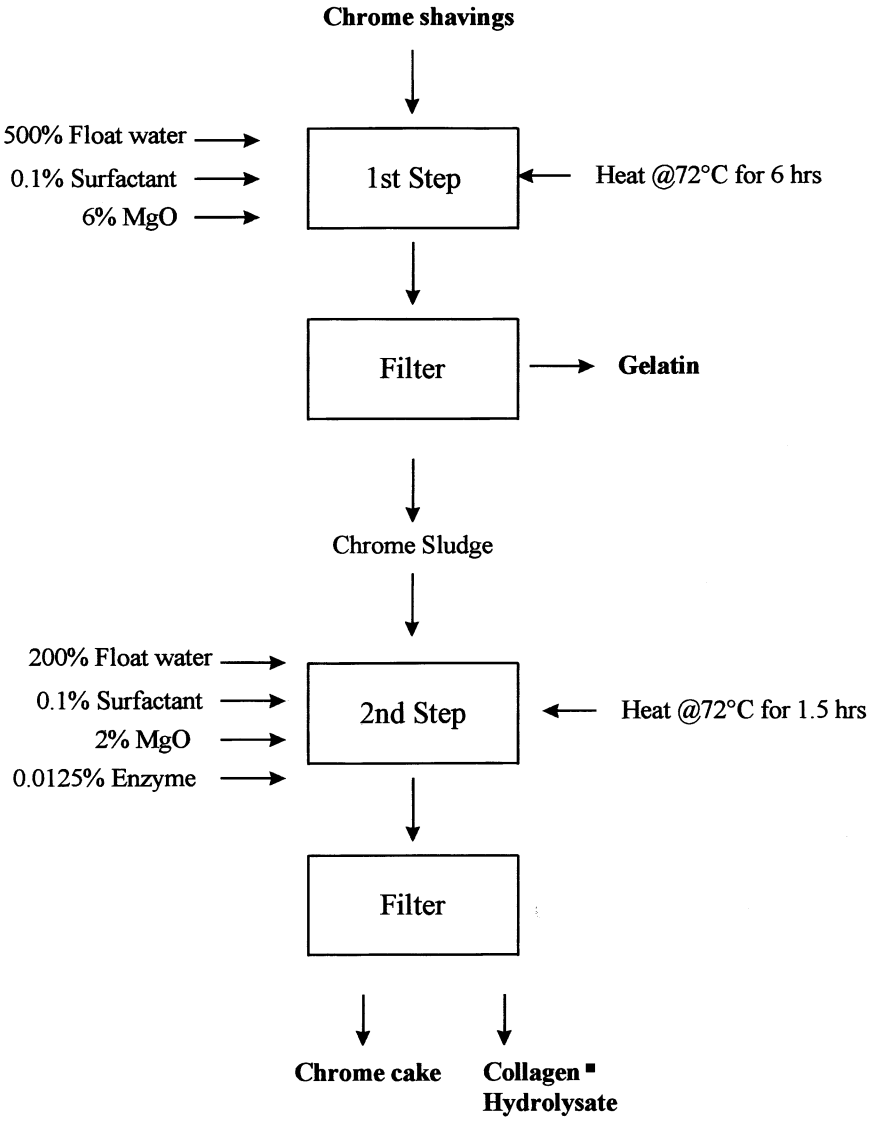
The treatment of the chrome cake is outlined in Fig. 3. The chrome cake was dissolved in concentrated sulfuric acid (23% on weight of initial chrome shavings) to give a pH of 1.0–1.2. The process was started in two large buckets outdoors, and finished in a conventional pilot plant tanning drum. Next, the pH was slowly raised to 1.9–2.1 by the addition of small aliquots of a 50% (w/w) solution of sodium hydroxide. The mixture was heated for 30 min at 60°C and allowed to stand overnight at room temperature. Organic materials were then removed from the chromium solution by filtration through Büchner porcelain funnels with Whatman #1 paper. The filtrate was adjusted to pH 9 with 50% (w/w) sodium hydroxide to precipitate the chromium. The solution containing suspended chromium was then heated, not to the boiling point as recommended by Okamoto [18], but to 70°C, the maximum temperature

for our tanning drum. The solution therefore was kept at this temperature for 2 h instead of 10 min [18], and was allowed to settle for 2 to 3 h. Chromic oxide was recovered from this mixture with a conventional filter press and washed with water.

2.4. *Analyses*

Chemical and physical properties of the gelatin, collagen hydrolysate and chrome cake were evaluated. Each sample was weighed and analyzed for moisture, ash, fat, protein as TKN and chromium. Moisture contents were determined by heating the samples at 105°C for 17 h. To determine the ash content, dried samples were further heated at 600°C for 2 h as previously described [19]. Chromium content was determined by atomic absorption spectrometry (Perkin-Elmer Atomic Absorption Spectrophotometer, Model 3300, Norwalk, CT). TKN was determined by the semi-micro Kjeldahl method; results were divided by the nitrogen content of collagen (18%) to give protein content. Fat was determined by extraction with chloroform as described previously [20].

The protein fractions were characterized functionally in terms of gel strength, dynamic viscosity and density on 6.67% (w/w) solutions. Gel strengths were obtained from Bloom determinations with a TA-XT2 Texture



% based on initial weight of chrome shavings

Fig. 2. Flow diagram of the procedure for treatment of chrome shavings.

Analyzer (Texture Technologies Corporation, Scarsdale, NY) [21]. Viscosities were measured at 60°C in a Cannon Manning viscometer [22]. Protein fractions were characterized structurally in terms of molecular weight ranges estimated by SDS–PAGE (polyacrylamide gel electrophoresis in sodium dodecyl sulfate) on 4–15% gels using a Phast-Gel System (Pharmacia Biotech Inc., Piscataway, NJ) [23]. The gels were scanned with a Personal Densitometer SI and analyzed using ImageQuaNT v:4.1 software (Molecular Dynamics, Inc., Sunnyvale, CA).

2.5. *Use of recovered chromium in tanning*

Chromic oxide ($Cr_2O_3 \cdot nH_2O$) dissolves readily in acid to form aquo ions, $[Cr(H_2O)_6]^{+3}$ that have only a very

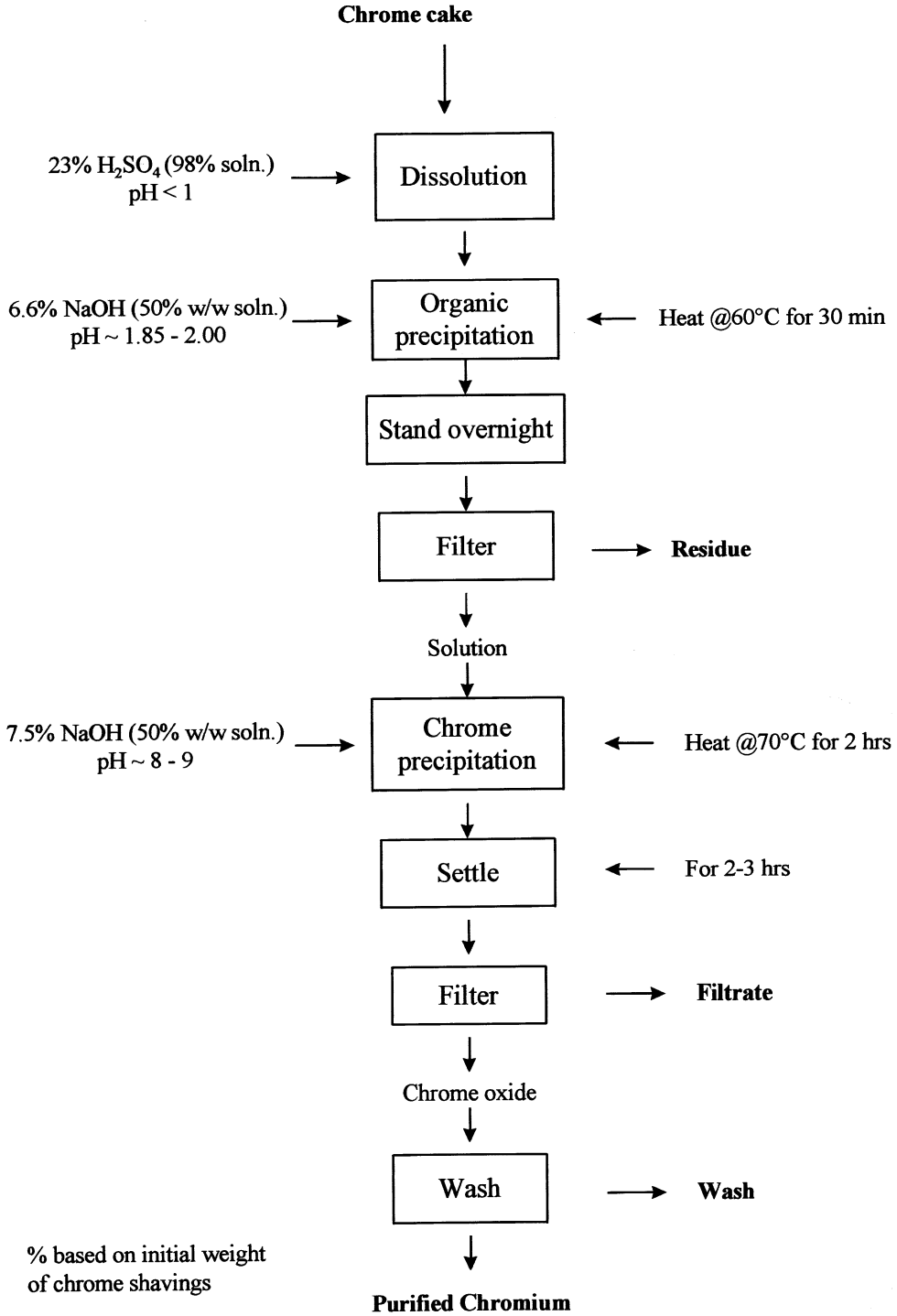


Fig. 3. Flow diagram of the procedure for purification of chrome cake.

slight tanning effect. Basic chrome sulfates, containing a mixture of hydroxyl and sulfate groups, are the preferred tanning agents. The tanning ability, often called the astringency, is related to the number of OH groups coordinated with the chromium. Above a basicity of approximately 57%, the chrome tanning materials start to become insoluble and precipitate. Thus, to prepare a model tanning bath, the purified chromic oxide was dissolved in sulfuric acid and the pH adjusted to 2.3. Approximately 3.6 kg sulfuric acid (4.0% on weight of initial chrome shavings) was needed to dissolve the chrome (30 g/l) and adjust the pH of the resulting solution. By diluting a portion of that solution, an artificial tanning bath could be prepared with a specified amount of chromium at a determined concentration. The tanning performance of the recovered chromium was evaluated by a matched sides trial on seven fresh cattle hides. One side of each hide was tanned with a commercial chrome tanning solution and the other with a tanning solution, containing from 0 to 100% recycled chromium. Each tanned side was subjected to standard measurements designed to evaluate the effectiveness of the tannage [13].

3. Results and discussion

As with any natural product, there may be considerable variation in the hides supplied to the tanner. In addition, each tanner will employ some individual variation of a conventional tanning process. Thus, one can expect the composition of chrome shavings to vary somewhat from batch to batch. Demonstrating the repeatability of the treatment process for chromium-containing leather waste on a pilot plant scale is an important step toward showing the viability of the process on an industrial scale. The work presented here includes the entire process, from the treatment of chrome shavings for protein isolation to the reuse of the recovered chromium in the tannery.

3.1. Protein products and chrome cake

The distribution of protein and chromium from shavings to the separated fractions of the process (outlined in Fig. 2) is summarized in Table 1. The recovery of protein into the gelatin and hydrolysate fractions is nearly quantitative, with approximately one third in the gelatin fraction and two thirds in the hydrolysate fraction. The recovery of purified chromium was slightly better than 50%.

The chemical and physical properties of the gelatin fraction, as extracted and after deionization, and those of the collagen hydrolysate are compared in Table 2. The properties of the extracted gelatin fraction are typical of commercial gelatins [24]. The weight average molecular weight of soluble collagen is about 280,000 D. Nearly half of the gelatin fraction has a molecular weight distribution above 85,000 D. Even in the collagen hydrolysate about 10% is in large fragments with the bulk in the lower, less than 50,000 D range. The ash content of deionized gelatin fractions was decreased significantly to less than 1%, well within the 0 to 3% range reported for technical grade gelatin [24]. The pH of the gelatin decreased until its isoionic point was reached, showing that deionization was complete. With deionization, the gel strength increased an average of about 135% and the viscosity about 22%, whereas the density decreased as was expected.

Chemical properties of the chrome sludge isolated after the extraction of gelatin, the chrome cake isolated after the hydrolysis step, and the purified chromic oxide are summarized in Table 3. The chrome cake retained

Table 1
Distribution of protein and chromium

Fraction	Protein	Chromium
Chrome shavings	360 (±30)	18 (±4)
Gelatin	109 (±10)	0.8 (±0.2)
Chrome sludge	251 (±20)	17 (±4)
Collagen hydrolysate	235 (±20)	0.15 (±0.05)
Chrome cake	15 (±4)	17 (±4)
Filtered residue	15 (±2)	5.5 (± 1.2)
Purified chromium	1.8 (±0.2)	9.5 (±2.0)

Values are means (range) obtained from four batches of shavings with three replicates per sample.
Protein and chromium concentrations are in g/kg of chrome shavings. Chromium concentrations are calculated as Cr_2O_3.

Table 2
Properties of protein fractions from a pilot plant process

Property	Gelatin	Deionized gelatin	Collagen hydrolysate
pH	9.1(0.1)	6.4(0.3)	9.6(0.2)
Total solids[a]	3.54(0.10)	2.56(0.14)	4.95(0.32)
Total ash[a,b]	17.33(0.87)	0.55(0.43)	4.37(0.43)
TKN[a,b]	17.35(0.87)	—	19.0(0.41)
Chromium (ppm),[b]	12.5(4.0)	11.8(5.0)	7.10(2.57)
Gel strength (g Bloom)	66.9(10.6)	167(16)	—
Dynamic viscosity (cP)	2.212(0.378)	2.866(0.444)	1.030(0.136)
Density	1.023(0.034)	0.992(0.009)	1.005(0.003)
Molecular weight distribution[c]			
> 208,000–85,000 D	47.0(5.5)		10.3[d]
85,000–50,000 D	22.1(1.0)		11.2
50,000– < 7,200 D	30.9(5.6)		78.5

Values are means, expressed as % (s. d.) from four batches of shavings, three replicates per sample.
[a] Expressed as %.
[b] Moisture free basis.
[c] Expressed as % of densitometer scan of coumassie blue stained Phast SDS gel.
[d] One analysis.

Table 3
Chemical properties of chrome fractions

Parameter	Chrome sludge		Chrome cake		Purified chromium	
Moisture	78.00	(0.98)	82.93	(0.51)	78.21	(0.51)
Total ash[a]	22.86	(0.62)	41.25	(0.59)	72.94	(0.44)
TKN[a,b]	14.65	(0.50)	10.88	(1.04)	2.20	(0.14)
Fat[a]	0.44	(0.17)	0.47	(0.10)	0.0023	(0.00)
Chromic oxide[a]	6.33	(0.41)	7.95	(1.04)	14.15	(0.48)

Values are means, expressed as % (s. d.) from four batches of shavings, three replicates per sample.
[a] Moisture free basis.
[b] Ash free basis.

Table 4
Composition of discharged fractions

Parameter	Residue	Filtrate	Wash
pH	–	9.10	8.20
Total solids	–	19.55(0.07)	10.47(0.04)
Moisture	60.35(0.41)	–	–
Total ash[a]	32.27(1.25)	81.95(0.47)	90.95(0.62)
TKN[a,b]	10.65(0.96)	8.24(0.20)	6.15(0.08)
Fat[a]	4.60(0.19)	–	–
Chromium[a]	0.68(0.00)	17.92(0.00)	14.33(0.00)

Values are average percents (s. d.) from four batches of shavings, three replicates per sample.
[a] Moisture free basis.
[b] Ash free basis.

more moisture than did the chrome sludge because the fibrous nature of the latter made it easier to filter. As one would expect, the ash content of the chrome cake increased and the TKN decreased as protein was removed during the enzymatic step of the procedure. The fat content was constant between the chrome sludge and the chrome cake, showing that the fat was not transferred to the protein fractions. The apparent increase in chromium from sludge to cake and purified chromic oxide is an artifact of the calculation as concentrations of other components are decreased. The recovery of chrome cake plus added reagents, at the point where the protein was filtered out of the chrome solution, was 96.6%. Overall, for the treatment of the chrome cake to remove protein and purify chromium in the oxide form, the recovery was greater than 95%. The purified chrome fraction was characterized by a low nitrogen content and essentially no fat. When this chromic oxide was used in a model tanning bath to replace commercial chrome at levels of 10 to 100%, the leather produced performed well in the standard tests of strength and stability [13].

3.2. *Residual materials from the process*

In the first step, chrome shavings were treated with MgO and water to produce gelatin in the filtrate and a residue of chrome sludge. The MgO was carried with the gelatin in the filtrate, when the gelatin was deionized to improve its physical properties, the MgO was transferred to the ion exchange resin. This resin would normally be regenerated for continued use. In the second step, the chrome sludge was treated with additional water, MgO and enzyme to produce a filtrate containing the collagen hydrolysate and chrome cake residue. No attempt was made to remove salts from the collagen hydrolysate; the salt (Mg) concentration is approximately one third that of the gelatin and would not interfere with use of the collagen hydrolysate. The compositions of residue, filtrate and wash resulting from the treatment of the chrome cake to produce purified chromic oxide are summarized in Table 4. On the basis of g/kg shavings, these results show that all the fat (5 g), along with approximately 15 g collagen and 5 g chrome, remain in the residue. Further processing of this residue might be warranted for a large scale operation. The combined filtrate and wash contain about 1.5 g chrome per kg shavings treated. Because the chrome is in the Cr(III) oxidation state, these fluid residuals are amenable to treatment in a typical waste water processing system.

3.3. *Economics of the process*

Capital and operating cost estimates for several variations of this process were made using the process simulation program ASPEN PLUS™. The model is available for evaluating additional variations [14]. The two-step treatment of chrome shavings to produce gelatin and collagen hydrolysate, combined with the third step to purify the chromic oxide was shown to be economically feasible. The most valuable product is the gelatin, the value of which increases directly with the increase in quality (higher gel strengths, Bloom values). As an example, a plant operating 24 h a day to process 20,000 lb (9000 kg) of chrome shavings could produce more than 900 kg of gelatin per day. The cost to produce partially evaporated gelatin would be about $0.52 per kg. Low quality gelatins (100 g Bloom) are available commercially for about $3.20 per kg [25]. Potential markets also exist for the collagen hydrolysate and purified chromium; the availability of a steady supply of products should help to turn potential markets into actual markets. Under current marketing conditions, one may expect the recovery of chromium and hydrolyzed collagen to be essentially revenue-neutral. The costs of recovering these components can be effectively offset by their sales, but these are not significant factors in determining the overall economic feasibility of the processes.

4. Conclusions

We have demonstrated that valuable products can be recovered from chrome shavings. A two-step process was used to extract the protein from the shavings, producing a technical gelatin and a collagen hydrolysate. The gelatin has potential use in cosmetics, adhesives, printing, photography, microencapsulation, films or even as an additive in finishing products for the leather industry. The collagen hydrolysate has potential uses as a fertilizer and in animal feed additives. In a third step, the cake remaining after the removal of protein was chemically treated to purify chromic oxide. This recovered chrome was suitable for use in further tanning operations. This economically feasible process provides a basis for a reduction in the amount of chromium-containing tannery waste going to landfills.

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